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Compositional Gradients in Petroleum Reservoirs

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Abstract

This paper describes methods for calculating the one-dimensional, vertical variation in composition with depth caused by gravity and thermal gradients. The Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) cubic equations of state (EOS) are used as thermodynamic models. Examples of calculated compositional gradients are given for reservoir fluid systems ranging from black oils to near-critical oils.

A solution algorithm is suggested for solving the isothermal gravity/chemical equilibrium (GCE) problem. The algorithm is simply an adaptation of a method proposed by Michelsen¹ for calculating saturation pressure. The problem of false (unstable) solutions is discussed, and the subsequent need for applying phase stability analysis to identify such false solutions. Finally, an algorithm is given for determining the location of a gas-oil contact (GOC).

A model for treating both gravity and thermal gradient has been used to quantify the potential effect of thermal diffusion on compositional grading. The model used was proposed by Belery and da Silva². Unfortunately, the physics and thermodynamics of thermal diffusion are not well understood. This model is only one of several approaches which have been suggested for treating thermal diffusion. Examples given in our paper show that thermal diffusion can have a marked effect on compositional grading, with the possibility of enhancing, reducing, or completely eliminating gradients caused by gravity alone.

We illustrate the potential danger of using gradient calculations for defining original hydrocarbon distributions (oil and gas in place) when limited fluid samples and PVT data are available. Furthermore, guidelines are given for when to use gradient calculations, and how to develop an EOS fluid characterization for reservoirs exhibiting compositional variation.

Introduction

The formulation for calculating compositional variation under the force of gravity for an *isothermal* system was first given by Gibbs. The condition of equilibrium is satisfied by the constraint

$$\mu_i(p^0, z^0, T) = \mu_i(p, z, T) + M_i g(h - h^0), \quad i=1, 2, \dots, N \quad (1)$$

where μ_i is the chemical potential of component i . z^0 is a homogeneous (single-phase) mixture at pressure p^0 at a reference depth h^0 . p is the pressure and z is the mixture composition at depth h . The entire system is at constant temperature ($dT/dh=0$).

In 1930, Muskat³ provided exact solutions to Eq. (1) for a simplified equation of state (ideal mixing). Numerical examples based on this oversimplified EOS led to the misleading conclusion that gravity has negligible effect on compositional variation in reservoir systems.

In 1938, Sage and Lacey⁴ evaluated Eq. (1) using a more realistic EOS model. The authors provide examples showing significant variations of composition with depth for reservoir mixtures. Furthermore, they made the key observation that systems in the vicinity of a critical condition should be expected to have significant compositional variations.

From 1938 until 1980 the petroleum literature is apparently void of publications regarding the calculation of compositional gradients. Several references during this period do, however, mention reservoirs exhibiting compositional variation. Most of these references are cited by Schulte⁵ in 1980.

Schulte appears to be the first to solve Eq. (1) using a cubic equation of state. This classic paper illustrates that significant compositional variation can result from gravity segregation in petroleum reservoirs. Schulte gives examples showing the effect of oil type (aromatic content) and interaction coefficients (used in the mixing rules of a cubic EOS) on compositional gradients. He also compares gradients calculated using the PR and SRK equations.

In 1980 significant compositional gradients were reported in the Brent field, North Sea.⁵⁻⁷ In the Brent formation of the Brent field a significant gradient in composition was observed, with the transition from gas to oil occurring at a *saturated GOC*. These papers also describe the unusual transition from gas to oil in the absence of a saturated gas-oil contact. The transition occurs instead at a depth where the reservoir fluid is a critical mixture, with a critical temperature equal to the reservoir temperature and a critical pressure less than the reservoir pressure (i.e. at an *undersaturated GOC*). Apparently the Statfjord formation in the Brent field is an example of a reservoir with an undersaturated GOC.

In 1983 Holt, Lindeberg, and Ratje⁸ presented a formulation of the compositional gradient problem including thermal diffusion. Example calculations in this paper were, unfortunately, limited to binary systems.

Numerous publications on the subject of compositional gradient were presented at SPE Technical Conferences in 1984 and 1985.^{9,10} Most of these were field case histories, and in fact a special session of the 1985 SPE Annual Technical Conference and Exhibition was dedicated to this subject.¹¹⁻¹³

Hirschberg⁹ discusses the influence of asphaltenes on compositional grading. He uses a simplified two-component model, with one component representing asphaltenes and the other representing the remaining deasphalted oil. The observation is made that compositional grading in heavier oils ($\gamma_G > 0.85$ or $\gamma_{API} < 35^\circ API$) can be strongly influenced by the *amount* and *properties* of asphaltenes. It is implied that quantitatively accurate estimates of compositional grading due to asphaltenes is extremely difficult because of the strong dependence of calculated results on physical properties of the oil and asphaltene(s). Finally, Hirschberg discusses two mechanisms for the development of a tar mat.

Riemens, Schulte, and de Jong¹⁰ present an interesting evaluation of the compositional grading in the Birba Field, Oman. It is shown, based on isothermal GCE calculations and field measurements of PVT data, that a significant compositional gradient exists. The authors also evaluate the possibility of injecting gas into the undersaturated oil zone where multicontact miscibility can develop.

Montel and Gouel¹⁴ suggest an algorithm for solving the isothermal GCE problem. The procedure is only approximate because it calculates pressure using an incremental hydrostatic term instead of solving for pressure directly. They discuss the effect of fluid characterization on compositional grading, and the effect of reservoir temperature and pressure. Finally, the authors suggest that including thermal diffusion may improve the reliability of calculated compositional gradients (though they choose not to include this effect in their study).

Metcalfe, Vogel, and Morris¹² report measured variation of composition and physical properties of reservoir fluids in the Anschutz Ranch East Field, Overthrust Belt (USA). These authors use an EOS to characterize the PVT behavior of the entire range of fluids sampled from the reservoir. However, instead of calculating the compositional variation using gravity/chemical equilibrium and the developed EOS characterization, they correlate compositional variation graphically based on measured data.

Creek and Schrader¹¹ report compositional grading data for another Overthrust Belt reservoir, the East Painter Field. Considerable data are presented, together with comparison of measured and calculated compositional gradients using the isothermal GCE model. They report difficulty in matching observed saturation pressure and GOR gradients. Finally, the authors indicate that most reservoirs along the Overthrust Belt have varying degrees of compositional grading.

Belery and da Silva² present a formulation describing the combined effects of gravity and thermal diffusion for a system of zero net mass flux. After assessing various approaches for treating thermal diffusion, they selected the method of Dougherty and Drickamer¹⁵. Belery and da Silva extend this formulation (which was originally valid only for binary systems) to multicomponent systems. A field example using EOS characterization and measured gradient data from the Ekofisk Field (North Sea) was used to illustrate the gravity/thermal model. Because measured PVT gradients were very scattered (probably due to sampling problems), the comparison is not quantitatively accurate (with or without thermal diffusion). However, the calculations show qualitatively the effect of thermal diffusion, and they are the first such calculations reported for multicomponent systems.

Wheaton¹⁶ discusses an isothermal GCE model including the influence of capillary pressure. The addition of capillary forces was apparently justified in an effort to assist in the initialization of reservoir simulators. Simulators use capillary pressure curves to initialize saturation and pressure distributions discretely in the vertical direction.

Results of the calculated examples in Wheaton's paper suggest that neglecting compositional variations in a gas condensate reservoir may result in potentially large errors in the initial hydrocarbons in place. *Obviously* these results are primarily a consequence of neglecting the compositional variation due to gravity/chemical equilibrium. Quantitatively similar results would have been obtained with or without the inclusion of capillary pressures.

Finally, Wheaton's observation that neglecting compositional gradients will lead to incorrect specification of initial oil and gas in place, is equally applicable to both gas condensate and oil reservoirs (i.e. practically any petroleum reservoir).

Chaback¹⁷, in his comments to Wheaton's paper, makes the observation that non-isothermal effects can be on the same order of magnitude as gravity effects. More importantly, he notes the fact that a non-isothermal system will never reach equilibrium (zero energy flux), even though a stationary (steady-state) condition of zero net mass flux is reached.

Montel¹⁸ gives a discussion of compositional grading, including comments about treating thermal diffusion. He provides an equation for calculating the Rayleigh-Darcy number which is used to indicate if a fluid/rock system will experience convection ("*mechanical instability*").

Pavel¹⁹ gives an extensive discussion and formal mathematical treatment of compositional grading, including gravity, thermal, and capillary forces. The treatment yields complicated expressions which, in a few cases, are solved for simple conditions (idealized EOS and binary systems). Many of the results are similar to those given by Muskat. No examples are given for multicomponent mixtures using a realistic thermodynamic model.

Recently, Faissat et al.²⁰ gave a theoretical review of equilibrium formulations including gravity and thermal diffusion. Most of the formulations are mentioned in the Belery and da Silva paper, though Faissat et al. formalize the thermal diffusion term in a generic way. Unfortunately, calculations are not provided for comparing the different formulations.

Isothermal Gravity/Chemical Equilibrium (GCE)

Eq. (1) gives the condition for *isothermal* gravity/chemical equilibrium (sometimes written in differential form as $du_i + M_i g dh = 0$, $i=1,2,\dots,N$). This condition represents N equations. Together with the constraint that the sum of mole fractions $z(h)$ must add to one,

$$\sum_{i=1}^N z_i f_i(h) = 1 \dots \dots \dots (2)$$

it is possible to solve for composition $z(h)$ and pressure $p(h)$ at a specified depth h .

Chemical potential can be expressed as $\mu_i = RT \ln f_i + \mu_i^*(T)$, where R is the gas constant, f_i is the fugacity (sometimes expressed in terms of the fugacity coefficient ϕ_i , where $f_i = \phi_i z_i p$), and $\mu_i^*(T)$ is the temperature-dependent ideal-gas contribution to chemical energy. Eq. (1) can now be expressed in terms of fugacity,

$$\ln f_i(p^0, z^0, T) = \ln f_i(p, z, T) + \frac{1}{RT} M_i g(h - h^0), \quad i=1, 2, \dots, N \dots \dots \dots (3)$$

For convenience we define $f_i(h) = f_i(p(h), z(h), T)$ and $f_i(h^0) = f_i(p^0, z^0, T)$, yielding

$$f_i(h) = f_i(h^0) \exp\left[-\frac{M_i g(h - h^0)}{RT}\right], \quad i=1, 2, \dots, N \dots \dots \dots (4)$$

The method of volume translation is widely used for correcting volumetric deficiencies of the original SRK and PR equations. The method involves calculating a linearly-translated volume v' by adding a constant c to the molar volume v calculated from the original EOS, $v' = v + c$. Peneloux et al.²¹ show that the volume shift modifies the component fugacity as $f_i^* = f_i \exp[c_i(p/RT)]$. This correction must be included in the fugacity expressions used for gradient calculations. The correction must also be included in the pressure derivative of fugacity used in the recommended algorithm for solving the isothermal GCE problem.

Based on the Gibbs-Duhem equation, it is guaranteed that combining the condition of mechanical equilibrium, $dp/dh = -\rho g$, with the condition of gravity/chemical equilibrium, Eq. (1), automatically satisfies the condition that

$$p(h) = p(h^0) + \int_{h^0}^h \rho(h) g dh \dots \dots \dots (5)$$

Interestingly, the isothermal GCE equations are still valid and satisfy this condition when a saturated gas-oil contact is located between h^0 and h (i.e. even when $p(h)$ is not a continuous function).

Isothermal GCE Algorithm

Eqs. (1) and (2) represent equations similar to those used to calculate saturation pressure. Michelsen¹ gives an efficient method for solving the saturation pressure calculation which has been modified here to solve the GCE problem,

$$Q(p, z) = 1 - \sum_{i=1}^N z_i [\tilde{f}_i(p^0, z^0) / f_i(p, z)] \dots \dots \dots (6)$$

$$= 1 - \sum_{i=1}^N Y_i$$

where

$$Y_i = z_i [\tilde{f}_i(p^0, z^0) / (f_i(p, z))] \dots \dots \dots (7)$$

$$\tilde{f}_i(p^0, z^0) = f_i(p^0, z^0) \exp\left[-\frac{M_i g(h - h^0)}{RT}\right] \dots \dots \dots (8)$$

An efficient algorithm for solving Eq. (6) uses a Newton-Raphson update for pressure and accelerated successive substitution (GDEM²²) for composition. The following procedure outlines this approach.

First calculate fugacities of the reference feed $f_i(p^0, z^0)$ and the gravity-corrected fugacity $\tilde{f}_i(p^0, z^0)$ from Eq. (8). This calculation needs to be made only once. Initial estimates of composition and

pressure at h are simply values at the reference depth, $z^{(1)}(h) = z^0$ and $p^{(1)}(h) = p^0$.

Calculate fugacities of the composition estimate z at the pressure estimate p . Calculate mole numbers from Eq. (7). Calculate fugacity ratio corrections,

$$r_i = \frac{\tilde{f}_i(p^0, z^0)}{f_i(p, z)} \left(\sum_{j=1}^N Y_j \right)^{-1} \dots \dots \dots (9)$$

Update mole numbers using

$$Y_i^{(n+1)} = Y_i^{(n)} [r_i^{(n)}]^\lambda \dots \dots \dots (10)$$

where four iterations use successive substitution ($\lambda=1$) followed by a GDEM promotion with λ given by

$$\lambda = \left| \frac{b_{11}}{b_{11} - b_{01}} \right| \dots \dots \dots (11)$$

$$b_{01} = \sum_{i=1}^N r_i^{(n)} r_i^{(n-1)}; \quad b_{11} = \sum_{i=1}^N r_i^{(n-1)} r_i^{(n-1)}$$

Calculate $z_i^{(n+1)}$ from $Y_i^{(n+1)}$ using

$$z_i = Y_i / \left(\sum_{j=1}^N Y_j \right) \dots \dots \dots (12)$$

Update the pressure estimate using a Newton-Raphson estimate,

$$p^{(n+1)} = p^{(n)} - \frac{Q^{(n)}}{(\partial Q / \partial p)^{(n)}} \dots \dots \dots (13)$$

where

$$\frac{\partial Q}{\partial p} = \sum_{i=1}^N Y_i r_i \left(\frac{\partial f_i / \partial p}{f_i(p, z)} \right) \dots \dots \dots (14)$$

Check for convergence using the following two tolerances

$$|1 - \sum_{i=1}^N Y_i| < 10^{-13} \dots \dots \dots (15)$$

$$\left(\sum_{i=1}^N \frac{\ln(r_i)}{\ln(Y_i / z_i)} \right)^2 < 10^{-8}$$

Iterate until convergence is achieved.

After finding the composition $z(h)$ and pressure $p(h)$ satisfying Eqs. (1) and (2), a phase stability test²³ must be made to establish if the solution is valid. A valid solution is single phase (thermodynamically *stable*). An *unstable* solution indicates that the calculated z and p will split into two (or more) phases, thereby making the solution invalid.

If the gradient solution is unstable, then the stability-test composition y should be used to reinitialize the gradient calculation. The starting pressure for the new gradient calculation can be p^0 , or preferably the converged pressure from the gradient calculation which lead to the unstable solution. Note that unstable gradient solutions usually occur only a short distance beyond a saturated GOC.

Locating A Gas-Oil Contact

Locating a potential GOC requires a trial-and-error search. For a saturated GOC, three approaches might be considered: (1) stability tests, (2) negative flash calculations²⁴, or (3) saturation pressure calculations. The first and second methods should be the fastest, with the negative flash probably being faster because information from previous flash calculations can be used for initialization of subsequent flash calculations.

Unfortunately, an algorithm based on either the stability test or negative flash results may suffer from the fact that *only* trivial

solutions exist over a large part of the reservoir thickness. On the other hand, once a non-trivial stability condition is found then either method can be used efficiently to determine the saturated GOC.

If an undersaturated GOC exists (i.e. a transition from gas to oil through a critical mixture), *only* a search based on saturation pressure calculations can be used. The following algorithm is recommended for locating both saturated and undersaturated GOCs.

First, calculate the composition and pressure at the top (z_T and p_T) and the bottom (z_B and p_B) of the reservoir, followed by the calculation of saturation pressures p_{sT} and p_{sB} . If the saturation types (bubblepoint/dewpoint) are the same at the top and bottom, then no GOC exists. Otherwise, a search for the GOC (h_{GOC}) is made.

A straight-forward search algorithm would be interval halving based on the saturation type. At iteration n , a solution with a dewpoint at depth $h^{(n)}$ would replace the top depth $h_T^{(n+1)}=h^{(n)}$ for the next iteration, and a solution with a bubblepoint at a given depth would replace the bottom depth $h_B^{(n+1)}=h^{(n)}$. The depth estimate for a given iteration is calculated from $h^{(n)}=0.5[h_B^{(n)}+h_T^{(n)}]$. The number of iterations required to meet a tolerance δh would be $1.5 \ln[(h_T-h_B)/\delta h]$. For example, only 13 gradient and saturation pressure calculations would be needed to achieve $\delta h=0.1$ m for a total thickness (h_T-h_B)=500 m.

More efficient algorithms for locating the GOC can probably be developed, particularly if a non-trivial stability solution can be located. Alternatively, Michelsen's critical point algorithm,²⁵ or his new method²⁶ for calculating accurate approximations for saturation pressure and temperature may provide a good starting point for developing an improved algorithm.

Example Applications

Four reservoir fluid systems are presented. Compositions and physical properties of oil samples from the four systems are given in **Table 1**. Reference conditions are also given. The oil samples represent four reservoirs in the North Sea. All but one example considers compositional variation both in the oil zone and an overlying gas zone.

The black oil (BO) and the slightly volatile oil (SVO) samples were characterized using the Pedersen et al.²⁷ procedure with 12 C_7+ fractions (SRK EOS). The volatile oil (VO) and near-critical oil (NCO) systems were characterized using the Whitson et al.²⁸⁻³⁰ procedures with 5 C_7+ fractions (PR EOS). EOS characterizations for the examples can be obtained from the author.

Black Oil Example

This example considers a saturated, low-GOR oil in equilibrium with a gas cap at initial reservoir conditions. Fig. 1 shows the saturation pressure variation with depth. Fig. 2 shows solution GOR as a function of depth.

The gradients in dewpoint and bubblepoint (expressed as a cumulative term $(p_{sGOC} - p_s)/(h_{GOC} - h)$) are about 0.045 bar/m and 0.03 bar/m, respectively (see Fig. 3). Interestingly, the dewpoint gradient is larger than the bubblepoint gradient.

Fig. 3 can be used for order-of-magnitude estimates of saturation pressure gradients. For example, the bubblepoint pressure of a "volatile oil" 100 m below a saturated GOC would be expected to have a bubblepoint about $(0.2 \text{ bar/m})(100 \text{ m})=20$ bar less than at the GOC; the value 0.2 bar/m was read from Fig. 3.

Perhaps the most interesting aspect of this example is the variation in GOR in the gas zone. The variation in composition is expressed in terms of liquid dropout curves in Fig. 4 ($T=5^\circ\text{C}$). Liquid dropout is an important fluid property for design and pressure-loss calculations in seabed pipelines.

For reservoir engineering purposes, this fluid system can be modelled as a dry gas with uniform composition in equilibrium with a constant-GOR (constant-bubblepoint) oil.

Slightly Volatile Oil Example

This example is taken from a reservoir with field data which suggested significant bubblepoint and solution-GOR variation with depth. Calculated results shown here are reasonably close to (but somewhat underpredict) observed variations.

The degree of undersaturation at reference depth of -2700 m was about 30 bar, as shown in Fig. 5. Solution GOR at the reference depth is about $150 \text{ Sm}^3/\text{Sm}^3$, compared with $180 \text{ Sm}^3/\text{Sm}^3$ at the GOC (Fig. 6). The variation in solution GOR in the oil zone has entered as a primary variable in the evaluation of miscible gas injection.

Liquid yield of the gas cap varies from $90 \text{ Sm}^3/\text{Sm}^3$ at the GOC to $75 \text{ Sm}^3/\text{Sm}^3$ 200 m above the GOC. Because the reservoir has significant dip, the variation in liquid yield in the gas cap has been an important factor in determining the initial condensate in place. Also, the phase behavior of mixing dry injection gas with a varying reservoir gas composition has required special attention (revaporization of liquid condensed upon mixing).

This example is used to study the importance of EOS fluid characterization on predicting compositional variation. To do so, it has been assumed that two production tests (DST 1 and DST 4) provided two insitu representative samples. DST 1 sampled an undersaturated reservoir oil, and DST 4 sampled an undersaturated reservoir gas. Compositions through C_{7+} , properties M_{7+} and γ_{7+} , and some PVT data were available for both samples (constant composition expansion data). The PVT "data" were generated using the same SRK EOS characterization used to generate the original compositional gradient.

The compositions and PVT data for the two samples were characterized with a single set of EOS properties for five C_7+ fractions using the PR EOS. Saturation pressures of the two samples were matched with the PR EOS characterization by modifying the C_1 - C_{7+} binary interaction parameters.

Isothermal gradient calculations were made using the DST 1 oil (-2700 m). Results are shown in Figs. 7 and 8. The GOC predicted was 5 m lower than the original ("true") GOC. Bubblepoint and dewpoint gradients are in good agreement with the original gradients. GOR is also in good agreement for the oil, and the slight error in GOR in the gas zone is due mostly to the difference in EOS predictions.

Isothermal gradient calculations were also made using the gas sampled from DST 4 (-2300 m). The same PR EOS characterization is used here as in the DST 1 oil calculations. Here the predicted GOC was 13 m too shallow (see Fig. 9). Predicted bubblepoint pressures are too low, mainly because the GOC is in error.

As seen in Fig. 10, the PR EOS overpredicts the GOR at the sampling depth even though the composition is exactly the same as predicted with the original SRK calculations. This simply indicates that the two EOS characterizations are different.

Fig. 11 shows predicted compositional gradients from the original SRK EOS characterization, and from the PR EOS characterization starting at both reference depths (DST 1 and DST 4). The largest discrepancies are oil compositions predicted from gradient calculations using DST 4 gas.

Fig. 12 shows the liquid dropout curve from a CVD experiment for gases at -2300 m (DST 4 sample depth). The original SRK and PR DST 4 samples are identical (through C_{7+}), and the difference in dropout curves stems solely from the EOS fluid characterizations. The gas predicted from the PR EOS using DST 1 sample and gradient calculations is not significantly different than the PR EOS prediction with the DST 4 gas sample (i.e. the correct gas composition).

We are currently studying how much PVT data and compositional information from the collected samples are required to tune the PR EOS characterization such that the DST 1 and DST 4 gradient predictions "overlay" the original SRK gradients.

Volatiles Oil Example

The current example is taken from the paper of Belery and da Silva. The reservoir oil is from the Ekofisk Field, North Sea. It is highly undersaturated (more than 100 bar), and fairly volatile with a solution GOR of about 300 Sm³/Sm³. The effects of thermal diffusion were made originally by Belery and da Silva, and are merely reproduced in this example.

Figs. 13-15 show the variation in bubblepoint, solution GOR, and composition with depth. The solid lines show results of the isothermal GCE calculations. Varying degrees of thermal diffusion are used by adjusting the Soret effect (thermal diffusion coefficient D_T).

The effect of thermal diffusion is dramatic on bubblepoint pressure, solution GOR, and composition. It appears that methane gradients are reduced (nearly reversed) at shallower depths, and greatly enhanced at depths below the reference depth. These trends are readily understood by studying the variation in thermal diffusion ratio k_T (Fig. 16). k_T is used in the relation for calculating the contribution to compositional gradient due to thermal diffusion,

$$\frac{dz_i}{dh} = -k_{Ti} \frac{d \ln T}{dh} \dots \dots \dots (16)$$

Below the reference depth the combined effect of large positive thermal diffusion ratios for methane and large negative thermal diffusion ratios for heavier components results in a significant reduction in methane content (and consequently, bubblepoint pressure and solution GOR; see Figs. 13 and 14).

Somewhat above the reference depth, thermal diffusion ratios are smaller by almost one order of magnitude. The direction of compositional gradient for methane is opposite to the gravity-induced gradient ($k_T < 0$), and the resulting methane concentration becomes almost constant for more than 200 m.

Near-Critical Oil Example

This example illustrates one of the most extreme conditions of compositional grading that can be expected in a reservoir system. The reservoir oil is near critical at the initial reference conditions (i.e. the oil critical temperature is only slightly greater than reservoir temperature). The reference oil is undersaturated by about 20 bar.

Figs. 17 and 18 show the saturation pressure and GOR variations with depth based on the isothermal GCE model. About 35 m above the reference depth an undersaturated GOC is found. A transition from oil to gas occurs through a critical mixture with a GOR of about 800 Sm³/Sm³. A very large gradient in GOR is seen in Fig. 18, with the maximum gradient occurring at the undersaturated GOC.

Figs. 19 and 20 show the same fluid system, but with a lower initial reference pressure of 469 bar (compared with 483 bar in Figs. 17 and 18). A near-critical saturated GOC is found about 10 m about the reference depth. Large saturation pressure and GOR gradients are observed near the GOC (similar to the slightly undersaturated system shown in Figs. 17 and 18). The saturation pressure gradient exceeds 1 bar/m near the GOC (see Fig. 3).

Degree of Undersaturation

The effect of higher initial reference pressure is shown in Figs. 21 and 22. For systems that are significantly undersaturated, the compositional gradients are greatly reduced. This is shown clearly in Fig. 23, where the saturation pressure gradient is plotted versus distance from the GOC.

The system having a slightly undersaturated GOC has similar gradients to the system with a near-critical saturated GOC, except very near the GOCs. The system with a saturated near-critical GOC has a gradient that approaches infinity at the GOC; the saturation pressure gradient for the system with a slightly undersaturated GOC drops abruptly to zero at the GOC. For the most undersaturated system in Fig. 23, saturation pressure gradient is fairly constant far away from the GOC, decreasing gradually towards a zero gradient at the GOC.

Effect of Heptanes-Plus Split

The effect of C_{7+} split on gradient calculations was studied for the slightly undersaturated near-critical oil. The number of C_{7+} components was varied from 5 to 25 using equal mass fractions with an exponential distribution (gamma distribution parameters $\alpha=1$ and $\eta=90$). Fig. 24 shows the resulting saturation pressure gradient. The dewpoint calculations are affected most, though still very little.

The isothermal gradient calculations using 25 C_{7+} fractions were analyzed to study the variation in molar distribution parameters as a function of depth. At each depth the calculated 25 C_{7+} mole fractions were fit to the gamma distribution model.^{29,31} The results are shown in Fig. 25, indicating that relatively small changes occur in the distribution parameters, even for this near-critical system. Similar analysis of the black-oil system was made with the result that distribution parameters in the oil and gas zones differ somewhat (e.g. $\alpha_g=0.6$ and $\alpha_o=1$), but they remain very constant within each zone.

Effect of Volume Translation

As mentioned earlier, the method of volume translation is used widely to improve volumetric predictions of the original SRK and PR equations of state. For most phase equilibria calculations (isothermal flash, stability test, and saturation pressure) this method has no effect on compositional results because the correction term $\exp[c_i(p/RT)]$ cancels.

For the GCE problem, fugacity of the reference mixture is at a different pressure than the mixture at depth h . The correction term does not therefore cancel. Fig. 26 shows the difference in gradient results with and without volume translation.

Effect of Passive Thermal Gradient

Faïssat et al.²⁰ define "passive thermal gradient" as the result of a system with thermal gradient but in the absence of thermal diffusion (obviously a theoretical system). Fig. 27 shows the results of passive thermal gradient. Dewpoint pressures are affected only slightly. In fact, compositional gradients are almost identical for the different thermal gradients, and the observed variation in saturation pressures are due almost entirely to the temperature dependence of saturation pressure.

Based on this example, it is reasonable to conclude that inclusion of a passive thermal gradient term in the gravity/chemical equilibrium model will have little effect. Furthermore, the introduction of such a term necessitates a numerical integration of the resulting equations. Because compositional gradients are not affected greatly by passive thermal gradients, even for this near-critical example, it doesn't seem worthwhile to abandon the isothermal GCE formulation which can be solved exactly.

Montel and Gouel¹⁴ suggest that after solving the isothermal GCE problem, that variation in properties such as saturation pressure be calculated including temperature variation. Although this appears to be a reasonable suggestion, it may cause problems for the initialization of a reservoir model that includes vertical temperature

variation (where the input composition-depth variation is based on isothermal GCE calculations).

Effect of Thermal Diffusion

Including a thermal diffusion contribution to the compositional gradient problem may result in non-physical solutions to the set of zero-mass-flux equations. The condition of mechanical stability (onset of convection) is given by a Rayleigh-Darcy number¹⁸ of 40. If mechanical instability is developed, the one-dimensional set of zero-mass-flux equations can no longer be used. Instead, a multidimensional treatment is required for the gravity/thermal problem including convection (requiring a numerical solution).

In this example the slightly undersaturated near-critical oil was subjected to varying degrees of thermal diffusion, with the results shown in Figs. 28 and 29. Fig. 28 shows the variation in saturation pressure versus depth. Not obvious from the figure is that a complete phase inversion occurs for the systems with 10% or more of the total thermal diffusion term. Phase inversion means that compositions above the reference depth are bubblepoint oils, and compositions somewhat below the reference depth are dewpoint gases (the "oil/gas" transition occurs at the maximum in saturation pressure).

Fig. 29 shows the reservoir pressure gradient (i.e. density) versus depth, indicating that non-physical solutions are obtained for the systems with 10% or more of the total thermal diffusion term. Obviously convection would be induced for systems with negative density gradients. Even the system with only 5% of the thermal diffusion term may experience convection if the Rayleigh-Darcy number exceeds 40 (even though the system has a positive density gradient).

Effect of Fluid Characterization

The slightly undersaturated near-critical oil was chosen to illustrate the importance of developing a comprehensive and consistent fluid characterization before making gradient calculations.

First, isothermal GCE calculations were made. Results are shown as solid lines in Figs. 30 and 31. These results and the properties of fluids at various depths calculated using the "original" PR EOS characterization (i.e. the one used to generate the compositional gradient) are assumed to represent "true" field data. These "data" are available from samples at three depths in the reservoir.

The three samples collected were (1) at the top of the reservoir (-2900 m), (2) in the middle of the reservoir (-3020 m), and (3) at the bottom of the reservoir (-3200 m). Exact compositional analyses through C_{7+} were obtained at each depth, together with properties M_{7+} and γ_{7+} . In this example, no "measured" PVT data were made available (i.e. properties calculated with the original PR EOS characterization).

Each sample was characterized *separately* using the SRK EOS with the Pedersen C_{7+} characterization procedure (the Pedersen splitting method does not allow several fluids to be characterized with a single set of EOS parameters).

The gradient calculations of the sampled gas at -2900 m predicted reasonably well both the dewpoint pressures and GORs above the datum depth. A saturated GOC was found at -3040 m. Predictions of oil properties below the GOC were not very accurate. Bubblepoints were overpredicted by 10 to 15 bar, while solution GORs were underpredicted by about 100 Sm^3/Sm^3 .

Gradient calculations using the critical mixture at -3020 m resulted in an undersaturated GOC slightly below the actual GOC. Dewpoint pressures are predicted reasonably well, even though GORs in the gas zone are underpredicted by several hundred Sm^3/Sm^3 . Below the GOC, bubblepoints were overpredicted and solution GORs were underpredicted.

For the sample taken at the bottom of the reservoir (-3200 m), gradient calculations gave very poor results. An undersaturated GOC was located at about the right depth, but with a saturation pressure 40 to 50 bar too low; GORs in the gas zone were severely underpredicted.

To obtain a consistent EOS characterization based on the three samples in this example, and eventually PVT data for these samples, a special characterization procedure must be followed. Only with a truly consistent characterization is it possible to reproduce the "true" compositional gradient and fluid properties of the original system. A procedure for developing such a fluid characterization is discussed below.

Developing an EOS Fluid Characterization

The recommended procedure for developing an EOS fluid characterization of a reservoir with compositional variation is based on obtaining a match of measured PVT data for several fluid samples. These fluid samples should cover the entire range of compositions which have been sampled from the reservoir.

The EOS characterization should consist of a *single* set of EOS parameters that apply to all fluid samples. The C_{7+} (C_{10+} , etc.) splitting procedure must be flexible enough to allow each sample to have different plus properties (e.g. M_{7+} and γ_{7+}), yet still resulting in a single set of common properties of the split fractions that apply to all samples. Whitson et al.²⁹ have developed a procedure specifically for this purpose.

The next step is to tune the EOS to measured PVT and compositional data. Critical properties of the C_{7+} fractions and binary interaction parameters are typically modified to improve the EOS match to measured data.

Having developed an EOS characterization that satisfactorily matches PVT data for all of the samples, isothermal gradient calculations can be made for each sample *separately*. Reference conditions (depth, pressure, and temperature) must be defined for each sample, a task which may be difficult because of multiple perforation intervals.

The gradient calculations from each sample should be compared. If the fluid gradients are similar (and hopefully similar to the measured gradient), then the EOS characterization is probably adequate. If the gradients from each sample are very different, several explanations can be given:

1. The EOS characterization is not sufficiently unique; i.e. it may fit all measured PVT data, but additional data covering a larger p-z space are needed to fine-tune the EOS.
2. The reference conditions are not sufficiently accurate. Reference depths are often difficult to define precisely.
3. The fluid samples are not in communication because of sealing faults or shale barriers. The fluids may not even have the same source rocks, in which case it may be impossible to determine a single EOS characterization that describes all fluids.
4. The isothermal (or non-isothermal) gradient model is not appropriate. Convective mixing may have occurred, regional temperature gradients may exist, etc.

It can be difficult to modify the EOS characterization to match measured PVT data from multiple samples in the reservoir, *and* to match measured variation of properties with depth. However, the task is more likely to succeed when both PVT *and* compositional data are

available for the samples included in the EOS tuning, and when these samples cover the entire range of compositions existing in the reservoir.

Conclusions

The following conclusions apply to results of compositional grading studies based on *isothermal* gravity/chemical equilibrium (GCE) calculations for reservoir fluids ranging from black oils to near-critical oils.

1. Expected gradients in saturation pressure range from 0.025 bar/m for black oils to a maximum of about 1 bar/m for near-critical oils approaching a GOC. Volatile systems exhibit large non-linear saturation pressure gradients, and particularly near a gas-oil contact. Black oil systems have nearly-constant saturation pressure gradients as a function of depth.

2. For systems exhibiting a GOC, the dewpoint and bubblepoint pressure gradients on each side of the GOC are nearly symmetric, with the dewpoint gradient usually being somewhat larger than the bubblepoint gradient. This applies to saturated GOCs and undersaturated GOC (where the transition from gas to oil occurs through a critical fluid).

3. Compositional grading is reduced significantly if the system is highly undersaturated. However, large compositional gradients may still exist for slightly undersaturated, near-critical systems. For most systems, gradients are inversely proportional to the degree of undersaturation.

4. The effect of EOS fluid characterization on compositional grading has been studied. It is recommended based on these results that the EOS tuning procedure should include all samples from the reservoir, or at least samples representing the entire range of compositions measured in the reservoir.

Furthermore, it is highly recommended that a *single* consistent set of EOS properties be determined such that PVT data from *all* samples are matched *simultaneously*. Only after such a tuning procedure can compositional gradient calculations be made reliably.

5. The effect of the number of C_{7+} fractions used in the EOS fluid characterization is insignificant when using five or more fractions, even for near-critical systems. Furthermore, the C_{7+} molar distribution changes very little as a function of depth, also for near-critical systems. For black-oil systems, the molar distribution in the gas zone may be different than the distribution in the oil zone, but in either zone the distributions remain constant.

6. In the absence of thermal diffusion effects, temperature gradients as high as 0.055°C/m resulted in insignificant compositional gradients compared with isothermal GCE calculations.

The following conclusions are based on studies of compositional grading in systems with temperature gradients where the effect of thermal diffusion, based on the model proposed by Belery and da Silva, is included in the analysis.

7. The tendency of thermal diffusion may be to enhance, reduce, balance, or completely reverse the compositional gradients calculated by a model based on isothermal gravity/chemical equilibrium.

Methane will migrate towards higher temperatures when the thermal diffusion ratio is negative.² This migration downwards is

opposite to the segregation of methane under gravity. The net result will be a reduced methane concentration gradient, and possibly even a gradient reversal.

Apparently, negative thermal diffusion ratios of methane are not uncommon. The tendency is for these ratios to increase with depth, eventually becoming positive and enhancing the methane gradient caused by gravity.

8. Significant methane movement downwards (caused by negative thermal diffusion ratios) will tend to create a mechanically unstable condition. The consequence may be convection. If convection occurs, the equilibrium problem is no longer one dimensional and another approach must be used for studying the compositional gradient problem.

9. There appears to be no consensus for how to formulate the non-isothermal gradient problem. Several adhoc approaches based on zero net flux have been suggested. Only one has been evaluated in this study. The alternative formulations should be tested, and perhaps the fundamental treatment of non-isothermal compositional gradients should be reexamined.

Nomenclature

b_{01}	coefficient in calculating λ
b_{11}	coefficient in calculating λ
c	volume shift parameter, $m^3/kmol$
D	molecular diffusion coefficient, m^2/s
D_T	thermal diffusion coefficient = Dk_T
f_i	fugacity of component i , Pa
g	acceleration due to gravity, m/s^2
h	vertical height, m
k_T	thermal diffusion ratio
M	molecular mass of component i , kg/kmol
M_{7+}	molecular mass of C_{7+} , kg/kmol
p	absolute pressure, Pa
p_b	bubblepoint pressure, Pa
p_d	dewpoint pressure, Pa
p_R	reservoir pressure, Pa
p_s	saturation pressure, Pa
Q	function for solving the GCE problem
r	fugacity ratio correction
R	universal gas constant
v	molar volume, $m^3/kmol$
v'	corrected molar volume, $m^3/kmol$
y	stability test phase molar composition
z	molar composition
α	shape factor in molar distribution model
γ_{API}	stock-tank oil specific gravity, °API
γ_o	stock-tank oil specific gravity, water=1
γ_{7+}	C_{7+} specific gravity, water=1
η	minimum molecular weight in molar distribution model
ρ	density, kg/m^3
λ	acceleration parameter in GDEM method
μ_i	chemical potential (Gibbs energy) of component i
μ_i^*	ideal-gas contribution to chemical potential of component i
ϕ_i	fugacity coefficient of component i

Subscripts

B	bottom of the reservoir
GOC	gas-oil contact
ref	reference condition

T top of the reservoir

Superscripts

o reference condition
n iteration counter

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References

1. Michelsen, M.L.: "Saturation Point Calculations," *Fluid Phase Equilibria* (1985) **23**, 181-192.
2. Belery, P. and da Silva, F.V.: "Gravity and Thermal Diffusion in Hydrocarbon Reservoirs," paper presented at the Third Chalk Research Program, June 11-12, Copenhagen (1990).*
3. Muskat, M.: "Distribution of Non-Reacting Fluids in the Gravitational Field," *Physical Review* (June 1930) **35**, 1384-1393.
4. Sage, B.H. and Lacey, W.N.: "Gravitational Concentration Gradients in Static Columns of Hydrocarbon Fluids," *Trans., AIME* (1938) **132**, 120-131.
5. Schulte, A.M.: "Compositional Variations within a Hydrocarbon Column due to Gravity," paper SPE 9235 presented at the 1980 SPE Annual Technical Conference and Exhibition, Dallas, Sept. 21-24.
6. Bath, P.G.H., Fowler, W.N., and Russell, M.P.M.: "The Brent Field, A Reservoir Engineering Review," paper EUR 164 presented at the 1980 SPE European Offshore Petroleum Conference and Exhibition, Sept. 21-24, London.
7. Bath, P.G.H., van der Burgh, J., and Ypma, J.G.J.: "Enhanced Oil Recovery in the North Sea," 11th World Petroleum Congress (1983).
8. Holt, T., Lindeberg, E., and Ratkje, S.K.: "The Effect of Gravity and Temperature Gradients on Methane Distribution in Oil Reservoirs," unsolicited paper SPE 11761 (1983).
9. Hirschberg, A.: "Role of Asphaltenes in Compositional Grading of a Reservoir's Fluid Column," *JPT* (Jan. 1988) 89-94.
10. Riemens, W.G., Schulte, A.M., and de Jong, L.N.J.: "Birba Field PVT Variations Along the Hydrocarbon Column and Confirmatory Field Tests," *JPT* (Jan. 1988) **40**, No. 1, 83-88.
11. Creek, J.L. and Schrader, M.L.: "East Painter Reservoir: An Example of a Compositional Gradient From a Gravitational Field," paper SPE 14411 presented at the 1985 SPE Annual Technical Conference and Exhibition, Las Vegas, Sept. 22-25.
12. Metcalfe, R.S., Vogel, J.L., and Morris, R.W.: "Compositional Gradient in the Anschutz Ranch East Field," paper SPE 14412 presented at the 1985 SPE Annual Technical Conference and Exhibition, Las Vegas, Sept. 22-25.
13. Montel, F. and Gouel, P.L.: "A New Lumping Scheme of Analytical Data for Compositional Studies," paper SPE 13119 presented at the 1984 SPE Annual Technical Conference and Exhibition, Houston, Sept. 16-19.
14. Montel, F. and Gouel, P.L.: "Prediction of Compositional Grading in a Reservoir Fluid Column," paper SPE 14410 presented at the 1985 SPE Annual Technical Conference and Exhibition, Las Vegas, Sept. 22-25.
15. Dougherty, E.L., Jr. and Drickamer, H.G.: "Thermal Diffusion and Molecular Motion in Liquids," *J. Phys. Chem.* (1955) **59**, 443.
16. Wheaton, R.J.: "Treatment of Variation of Composition With Depth in Gas-Condensate Reservoirs," *SPE* (May 1991) 239-244.
17. Chaback, J.J.: "Discussion of Treatment of Variations of Composition With Depth in Gas-Condensate Reservoirs," *SPE* (Feb. 1992) 157-158.
18. Montel, F.: "Phase Equilibria Needs for Petroleum Exploration and Production Industry," *Fluid Phase Equilibria* (1993) No. 84, 343-367.
19. Pavel, B.: *Mathematical Theory of Oil and Gas Recovery*, Petroleum Engineering and Development Studies, No. 4, Cluwer Academic, Dordrecht (1993).
20. Faissat, B., Knudsen, K., Stenby, E.H., and Montel, F.: "Fundamental Statements about Thermal Diffusion for a Multicomponent Mixture in a Porous Medium," *Fluid Phase Equilibria (submitted)* (1994).
21. Peneloux, A., Rauzy, E., and Freze, R.: "A Consistent Correction for Redlich-Kwong-Soave Volumes," *Fluid Phase Equilibria* (1982) **8**, 7-23.
22. Crowe, A.M. and Nishio, M.: "Convergence Promotion in the Simulation of Chemical Processes: The General Dominant Eigenvalue Method," *AIChE J.* (1975) **21**, 528-533.
23. Michelsen, M.L.: "The Isothermal Flash Problem. Part I. Stability," *Fluid Phase Equilibria* (1982) **9**, 1-19.
24. Whitson, C.H. and Michelsen, M.L.: "The Negative Flash," *Fluid Phase Equilibria* (1989) **53**, 51-71.
25. Michelsen, M.L.: "Calculation of Critical Points and Phase Boundaries in the Critical Region," *Fluid Phase Equilibria* (1984) **16**, 57-76.
26. Michelsen, M.L.: "A Simple Method for Calculation of Approximate Phase Boundaries," *Fluid Phase Equilibria (submitted)* (1994).
27. Pedersen, K.S., Thomassen, P., and Fredenslund, A.: "Characterization of Gas Condensate Mixtures," *C₇₊ Fraction Characterization*, L.G. Chorn and G.A. Mansoori (ed.), Advances in Thermodynamics, Taylor & Francis, New York (1989) **1**.
28. Whitson, C.H. and Brule, M.R.: *Phase Behavior*, Monograph, SPE of AIME, Dallas (1994) (in print).
29. Whitson, C.H., Andersen, T.F., and Soreide, I.: "C₇₊ Characterization of Related Equilibrium Fluids Using the Gamma Distribution," *C₇₊ Fraction Characterization*, L.G. Chorn and G.A. Mansoori (ed.), Advances in Thermodynamics, Taylor & Francis, New York (1989) **1**, 35-56.
30. Soreide, I.: "Improved Phase Behavior Predictions of Petroleum Reservoir Fluids From a Cubic Equation of State," Dr. Ing. thesis, IPT Report 1989:4, Norwegian Institute of Technology, Department of Petroleum Engineering and Applied Geophysics (1989).
31. Whitson, C.H., Anderson, T.F., and Soreide, I.: "Application of the Gamma Distribution Model to Molecular Weight and Boiling Point Data for Petroleum Fractions," *Chem. Eng. Comm.* (1990) **96**, 259-278.

* Ref. 2 can be obtained from C. Whitson, Dept. Pet. Eng., U. Trondheim, NTH, 7034 Trondheim, Norway.

**TABLE 1 - COMPOSITIONS, PROPERTIES, AND
REFERENCE CONDITIONS OF EXAMPLE RESERVOIR FLUIDS**

MOLAR COMPOSITIONS & PHYSICAL PROPERTIES				
Component/ Property	Black Oil	Slightly Volatile Oil	Volatile Oil	Near Critical Oil
N ₂	0.262	0.270	0.930	0.550
CO ₂	0.367	0.790	0.210	1.250
C ₁	35.193	46.340	58.770	66.450
C ₂	3.751	6.150	7.570	7.850
C ₃	0.755	4.460	4.090	4.250
iC ₄	0.978	0.870	0.910	0.900
C ₄	0.313	2.270	2.090	2.150
iC ₅	0.657	0.960	0.770	0.900
C ₅	0.152	1.410	1.150	1.150
C ₆	1.346	2.100	1.750	1.450
F ₁	4.779	3.297	5.381	4.885
F ₂	4.374	2.981	5.866	3.200
F ₃	4.003	2.696	5.003	2.300
F ₄	10.084	6.633	3.519	1.663
F ₅	7.728	3.430	1.992	1.052
F ₆	5.922	4.008		
F ₇	4.538	2.072		
F ₈	4.445	3.079		
F ₉	3.117	2.058		
F ₁₀	3.020	1.641		
F ₁₁	2.527	1.493		
F ₁₂	1.689	0.991		
Total	100.000	100.000	100.000	100.000
C ₇₊	56.226	34.380	21.760	13.100
M ₇₊	243.0	225.0	228.0	220.0
γ ₇₊	0.8910	0.8700	0.8559	0.8400
Reference Conditions				
h ^o (m)	1550	2635	3160	3049
T (°C)	68	95	130	132
p ^o (bara)	160	263	492	483/469
p _b (bara)	160	246	383	462
GOR ^a (Sm ³ /Sm ³)	62	156	299	560
γ _o ^a	0.887	0.860	0.825	0.827

a. Single-stage separator.

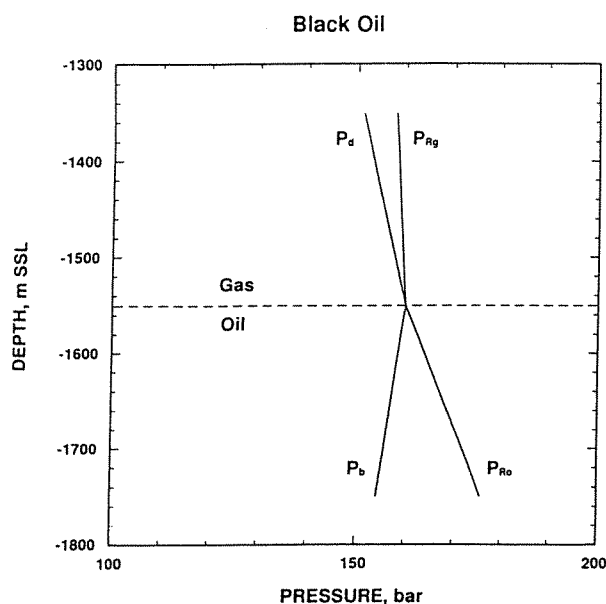


Fig. 1 Saturation pressure variation for Black Oil system using isothermal GCE.

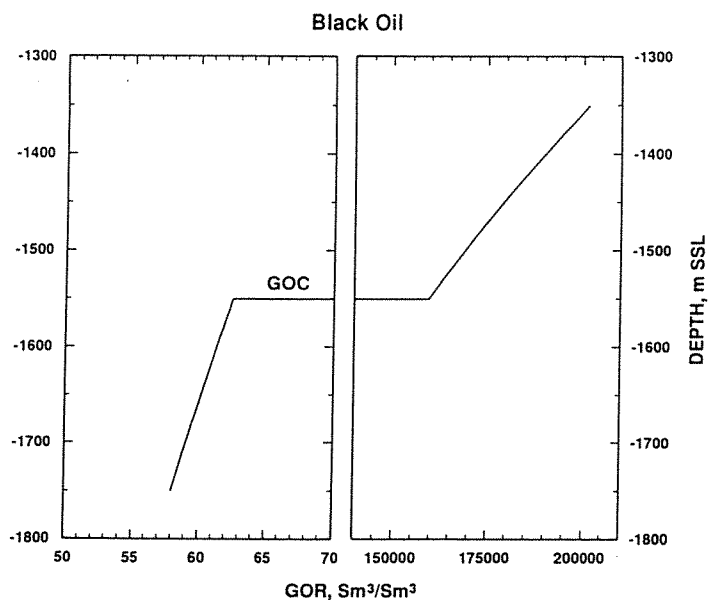


Fig. 2 Gas-oil ratio variation for Black Oil system using isothermal GCE.

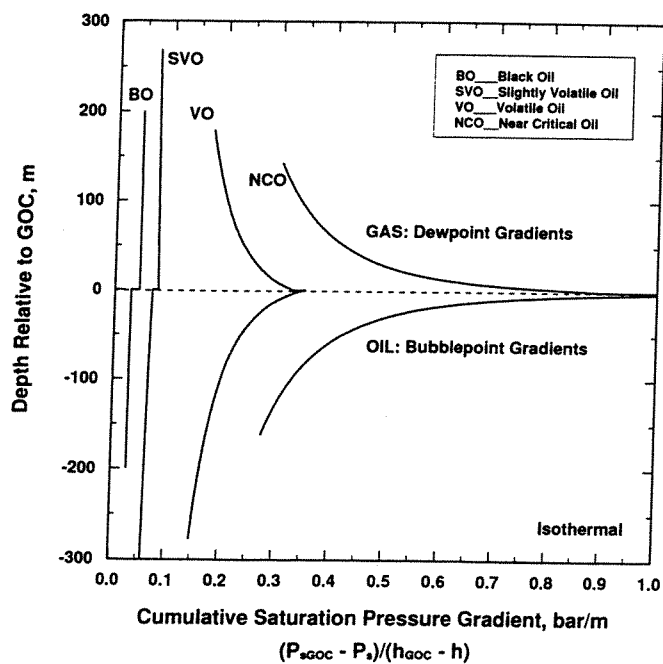


Fig. 3 Cumulative saturation pressure gradient versus depth relative to saturated GOC.

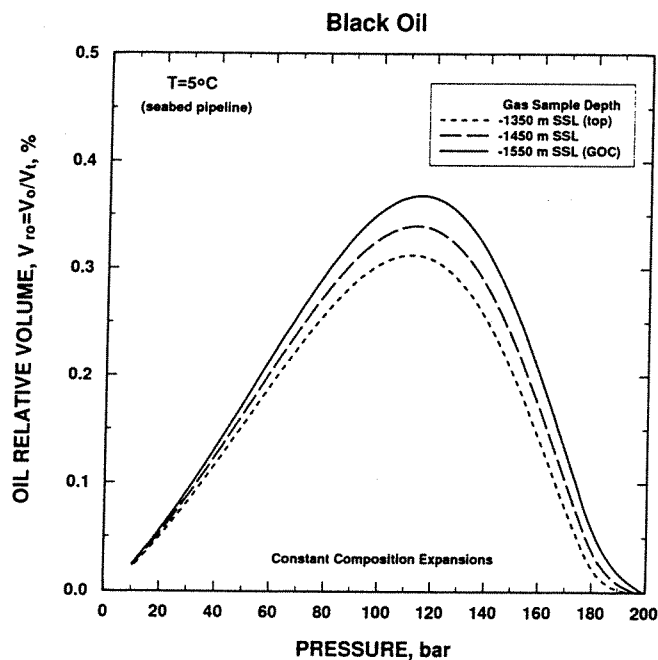


Fig. 4 Liquid dropout curves for reservoir gases at various depths for Black Oil system.

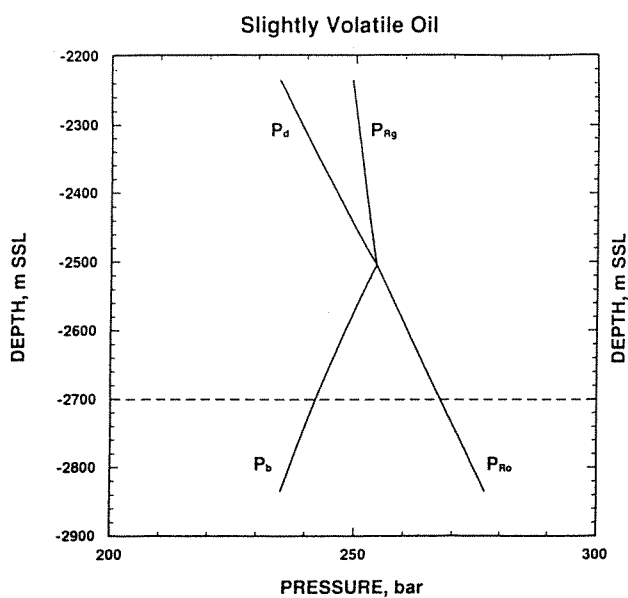


Fig. 5 Saturation pressure variation for Slightly Volatile Oil system using isothermal GCE.

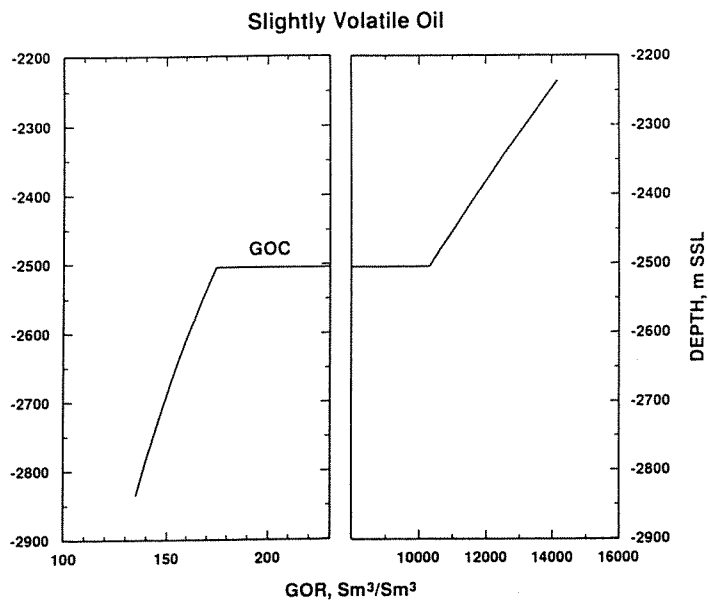


Fig. 6 Gas-oil ratio variation for Slightly Volatile Oil system using isothermal GCE.

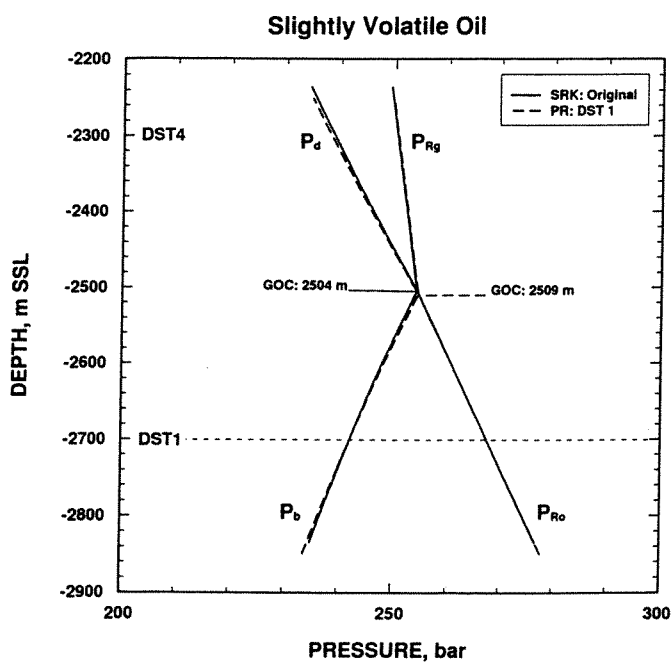


Fig. 7 Comparison of saturation pressure variation for original SVO fluid and the DST 1 sample.

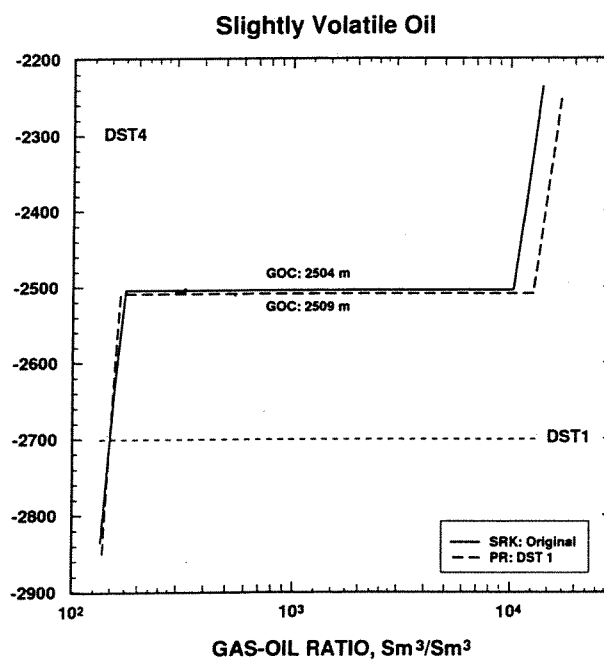


Fig. 8 Comparison of gas-oil ratio variation for original SVO fluid and the DST 1 sample.

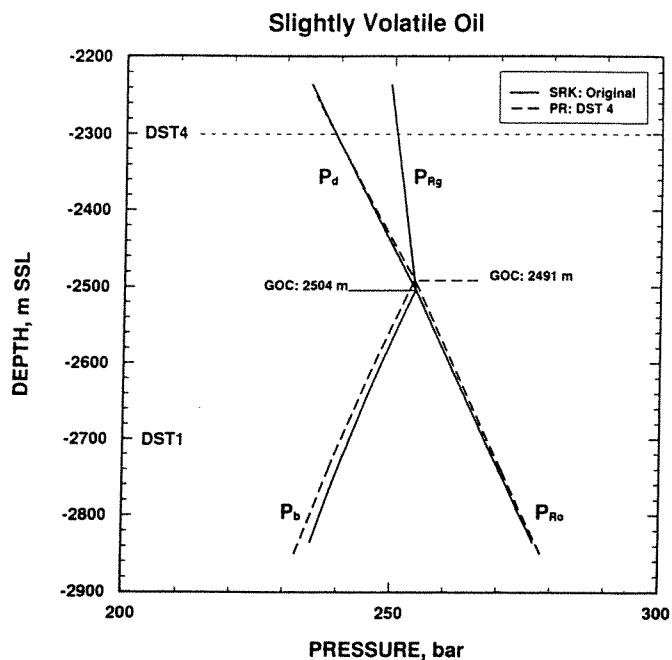


Fig. 9 Comparison of saturation pressure variation for original SVO fluid and the DST 4 sample.

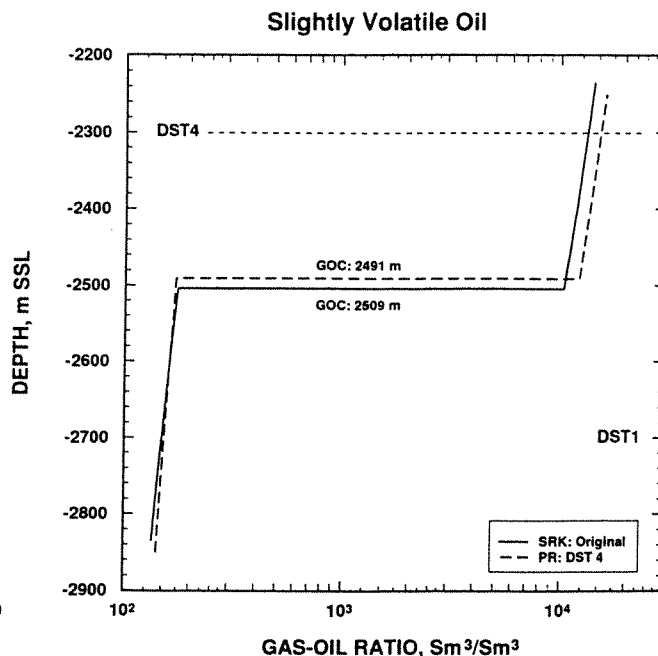


Fig. 10 Comparison of saturation pressure variation for original SVO fluid and the DST 4 sample.

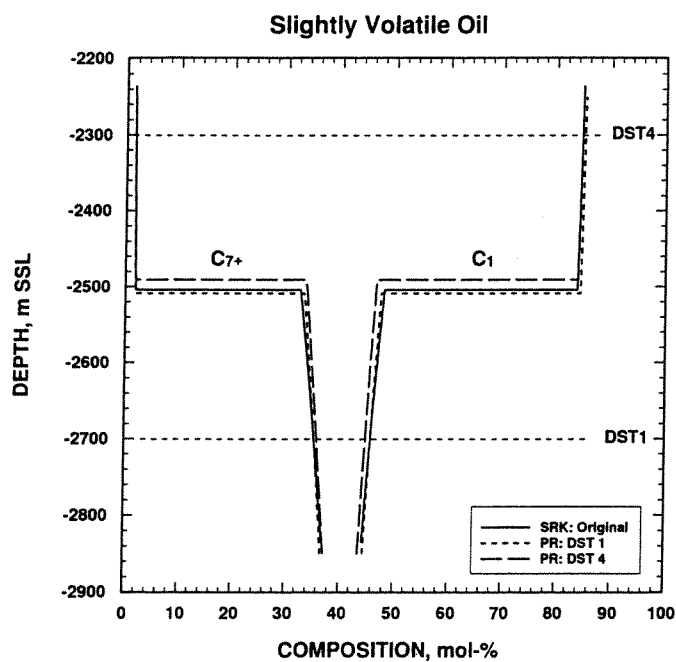


Fig. 11 Comparison of methane and C_{7+} compositional variation for original SVO fluid and the DST 1 & 4 samples.

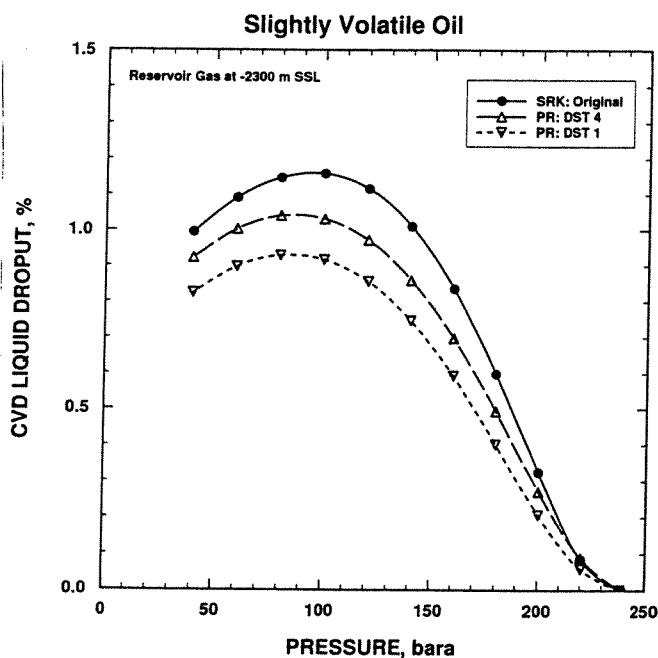


Fig. 12 Comparison of liquid dropout curves of reservoir gas at -2300 m for original SVO fluid and the DST 1 & 4 samples.

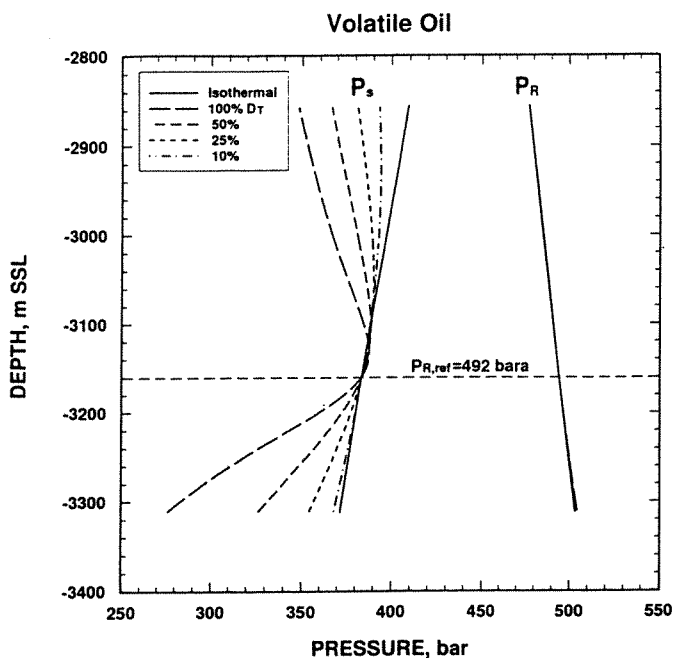


Fig. 13 Effect of thermal diffusion on saturation pressure variation for Volatile Oil system.

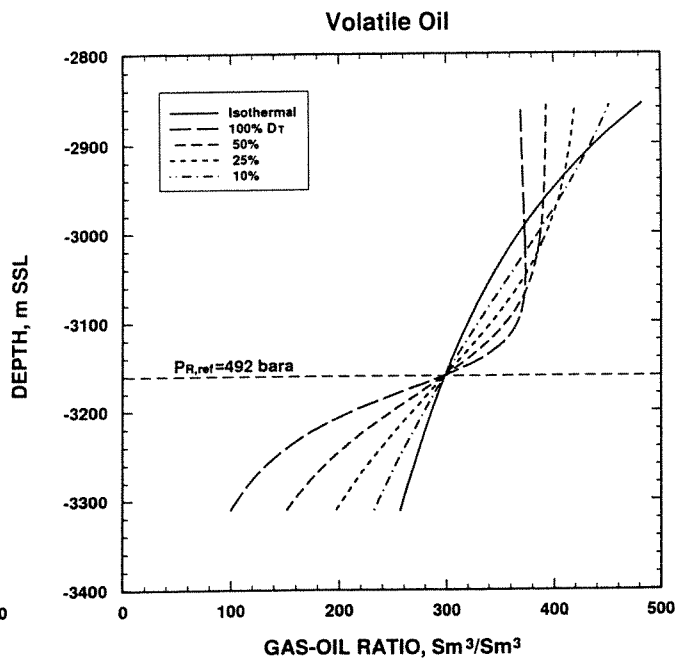


Fig. 14 Effect of thermal diffusion on gas-oil ratio variation for Volatile Oil system.

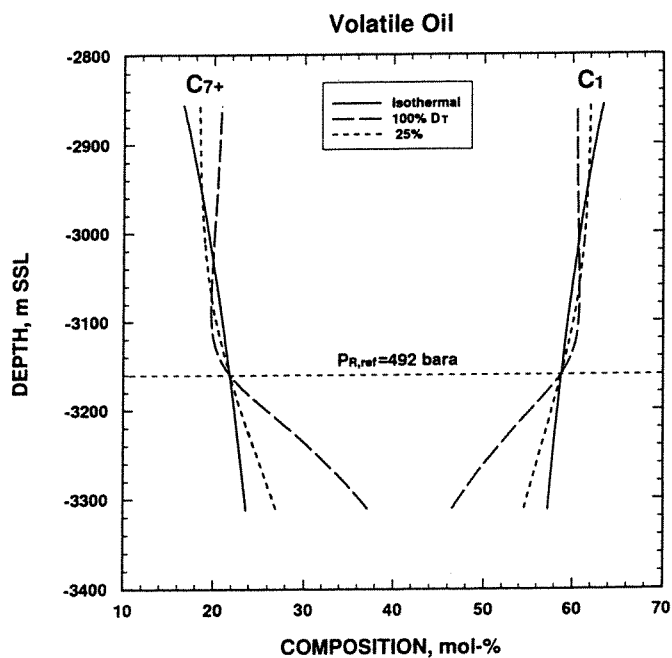


Fig. 15 Effect of thermal diffusion on methane and C_{7+} compositions for Volatile Oil system.

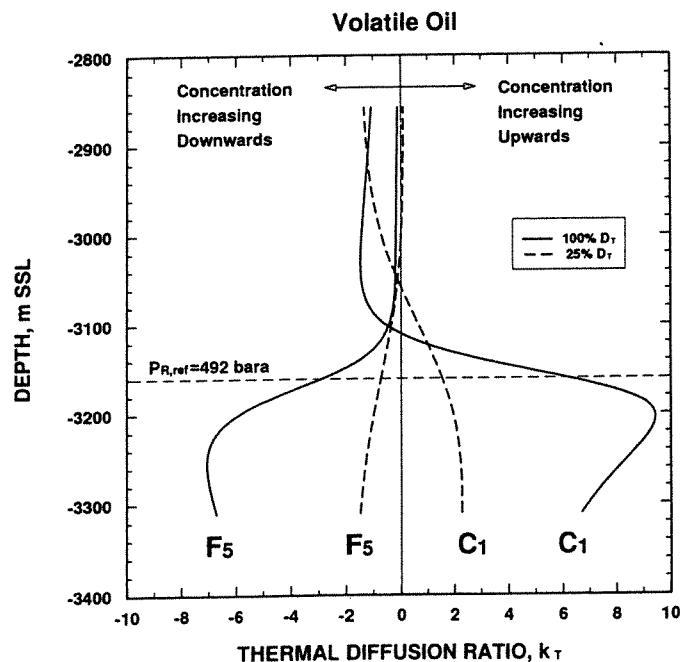


Fig. 16 Variation in thermal diffusion ratio for methane and heaviest C_{7+} fraction (F_5) for Volatile Oil system.

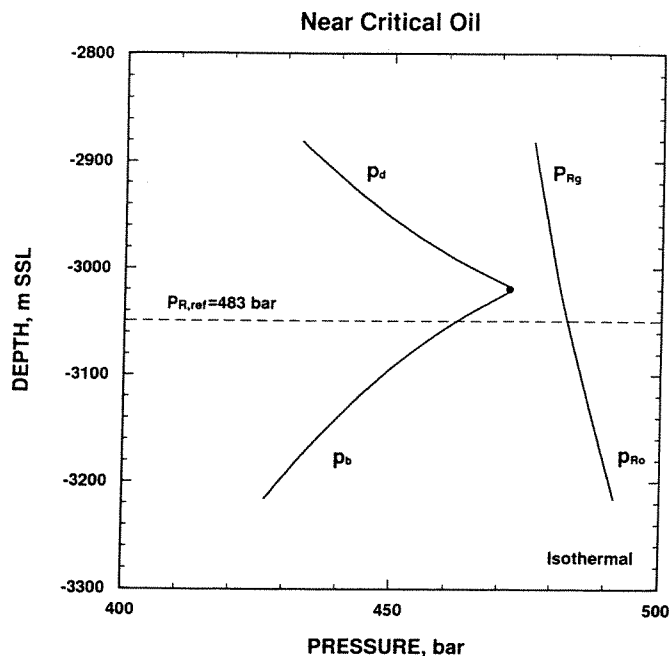


Fig. 17 Saturation pressure variation for Near Critical Oil system using isothermal GCE; slightly undersaturated GOC.

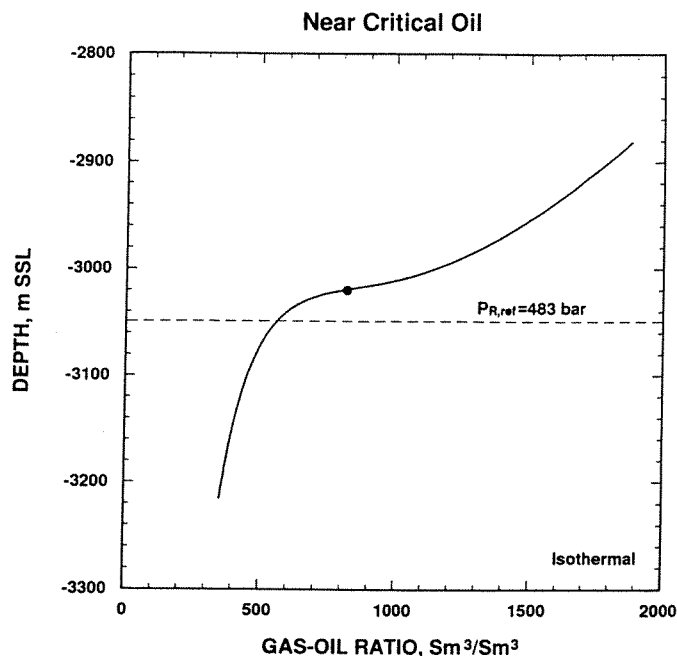


Fig. 18 Gas-oil ratio variation for Near Critical Oil system using isothermal GCE; slightly undersaturated GOC.

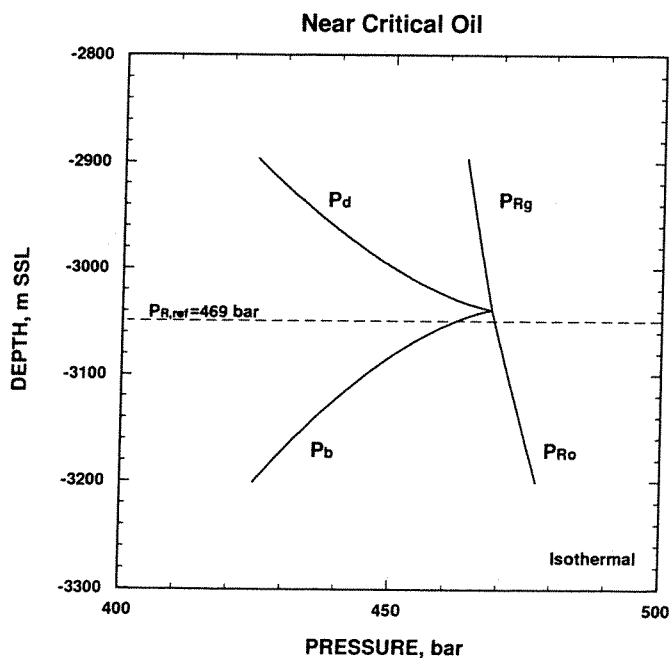


Fig. 19 Saturation pressure variation for Near Critical Oil system using isothermal GCE; saturated GOC.

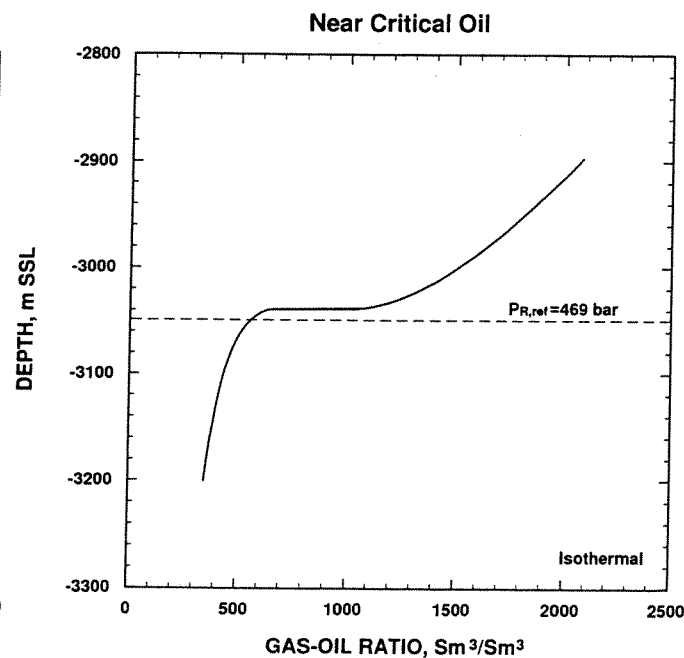


Fig. 20 Gas-oil ratio variation for Near Critical Oil system using isothermal GCE; saturated GOC.

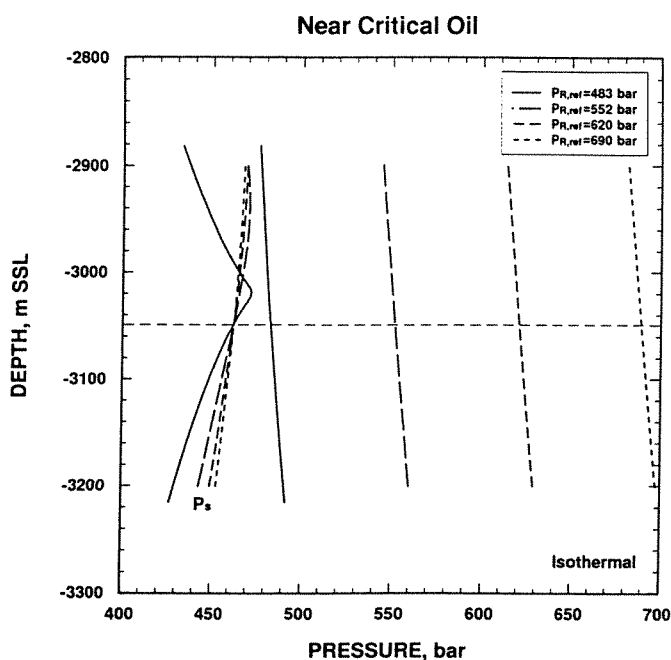


Fig. 21 Effect of degree of undersaturation on saturation pressure gradient for Near Critical Oil system using isothermal GCE.

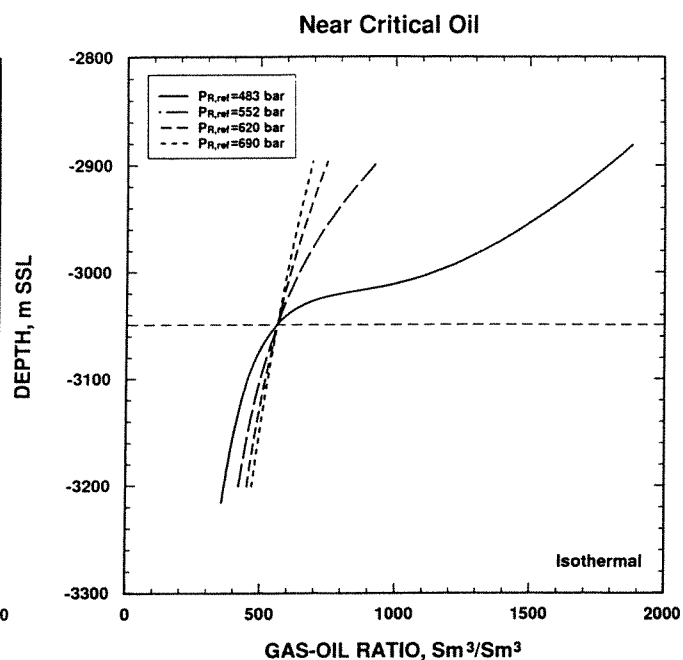


Fig. 22 Effect of degree of undersaturation on gas-oil ratio gradient for Near Critical Oil system using isothermal GCE.

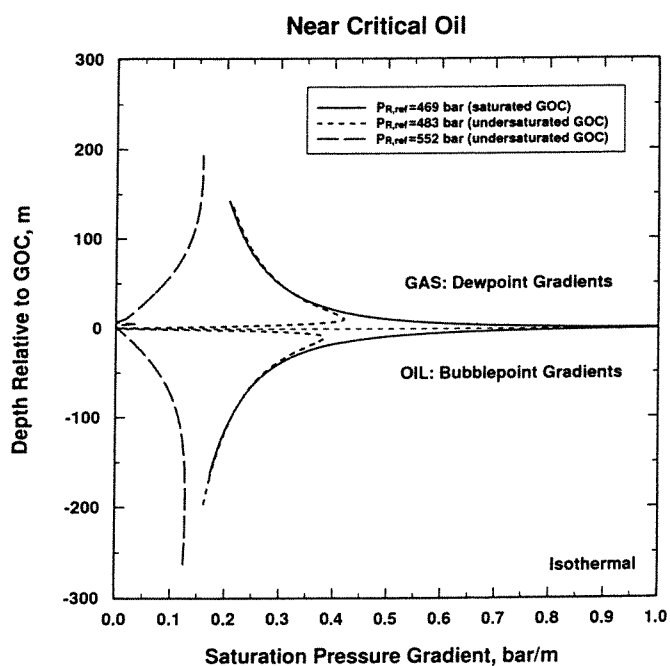


Fig. 23 Saturation pressure gradient versus depth relative to GOC for Near Critical Oil system at varying degrees of undersaturation.

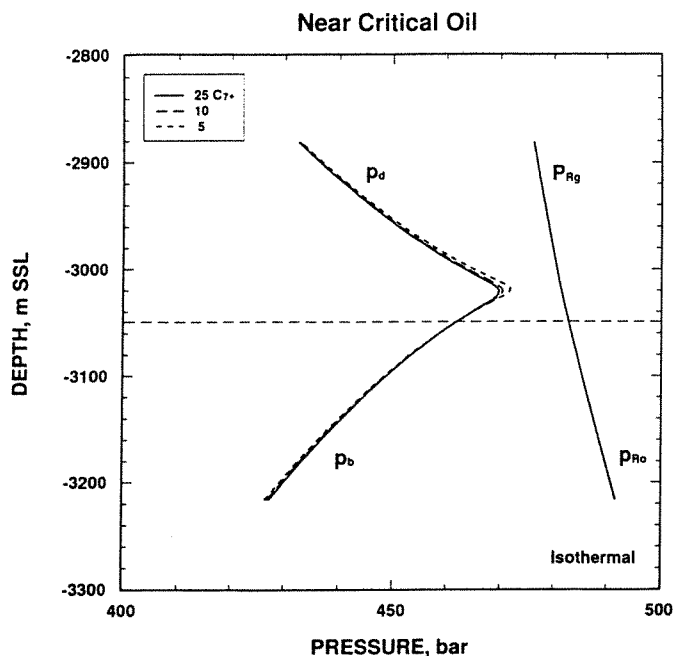


Fig. 24 Effect of number of C_{7+} fractions on the saturation pressure variation for NCO system using isothermal GCE; slightly undersaturated GOC.

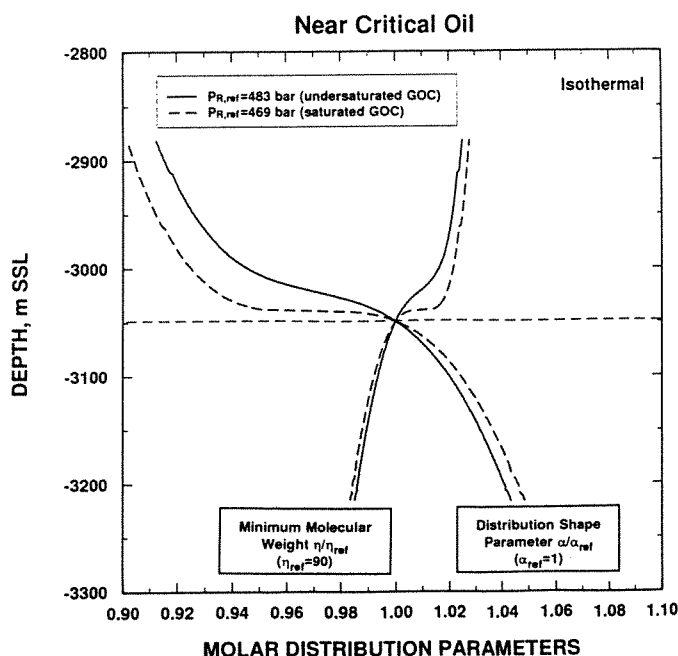


Fig. 25 Variation of molar distribution parameters for NCO system using isothermal GCE; slightly undersaturated GOC.

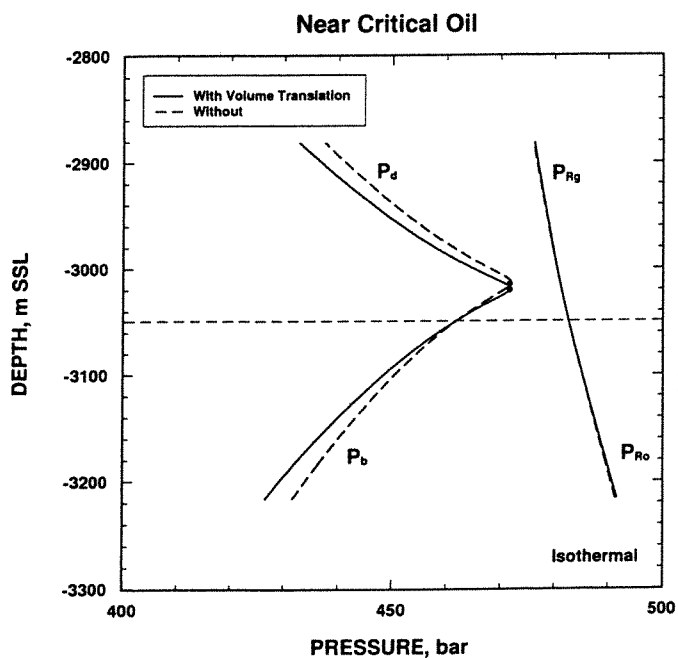


Fig. 26 Effect of volume translation on the saturation pressure variation for NCO system using isothermal GCE; slightly undersaturated GOC.

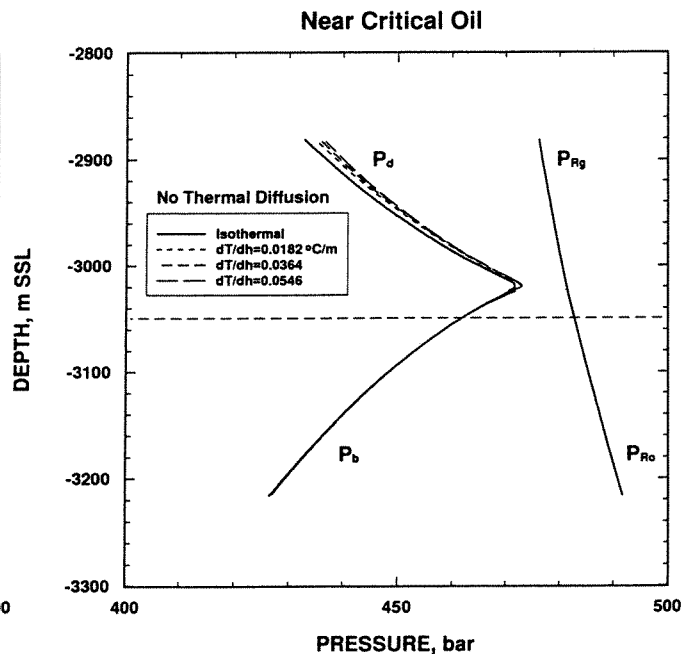


Fig. 27 Effect of passive thermal gradient on the saturation pressure variation for NCO system using isothermal GCE; slightly undersaturated GOC.

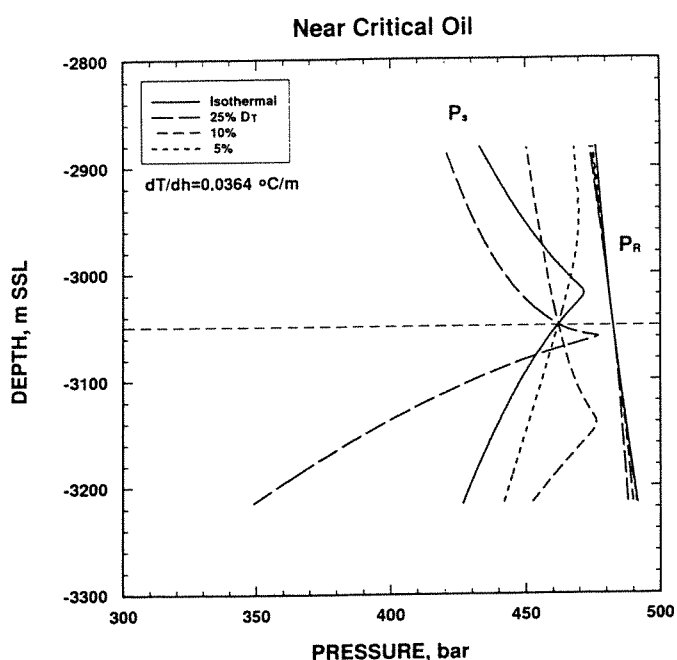


Fig. 28 Effect of thermal diffusion on saturation pressure variation for NCO system; slightly undersaturated GOC.

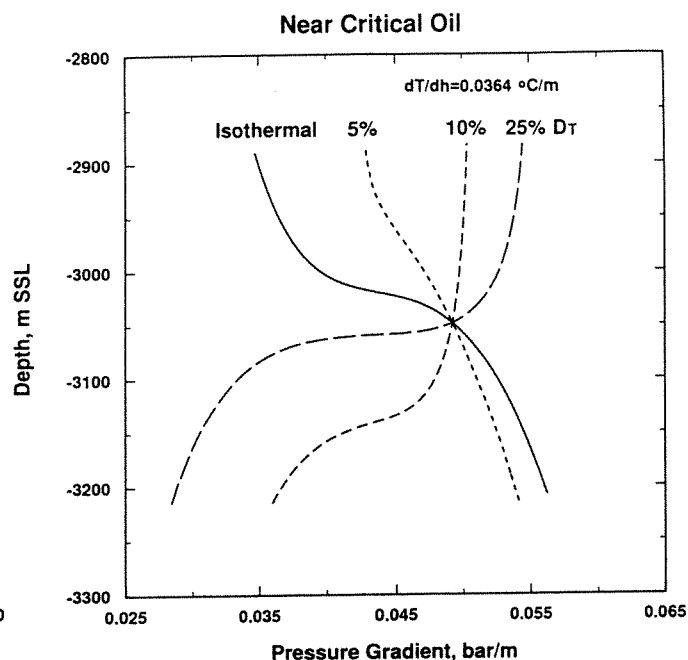


Fig. 29 Variation in pressure gradient (density) for different degrees of thermal diffusion for NCO system.

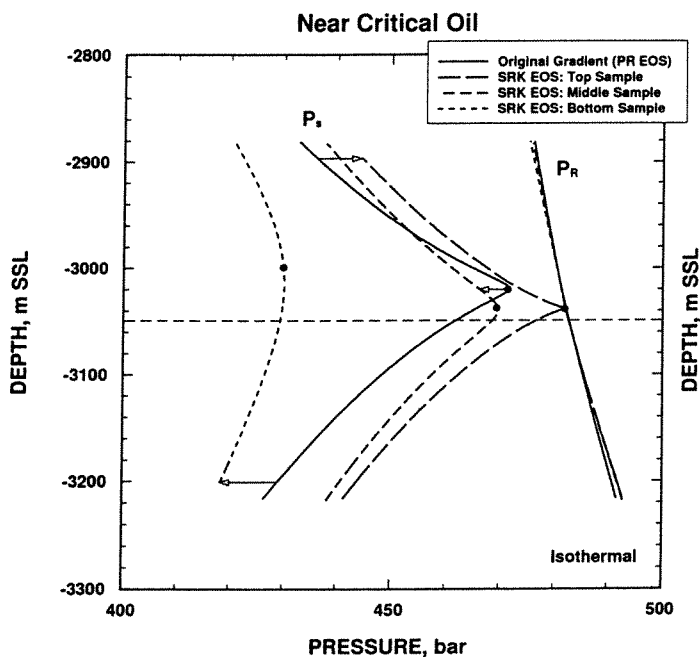


Fig. 30 Saturation pressure variation for original NCO system and for samples taken at different depths.

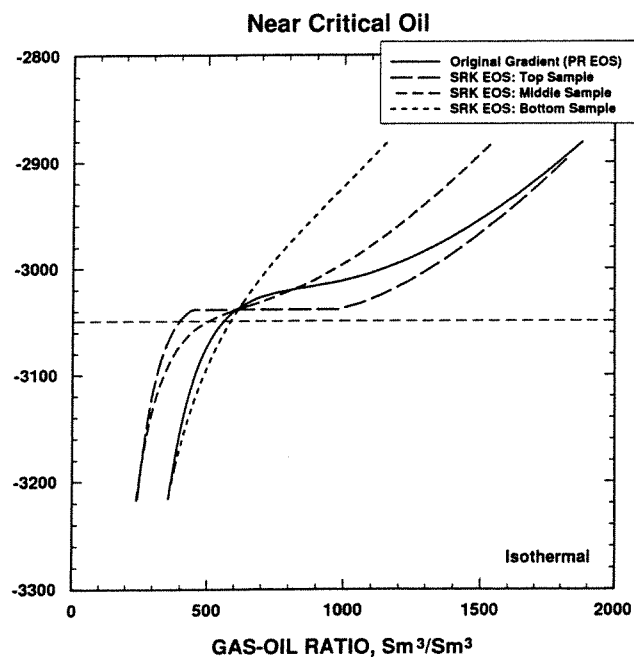


Fig. 31 Gas-oil ratio variation for original NCO system and for samples taken at different depths.